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CLAIM + DETAILED DESCRIPTION

[Claim(s)]

[Claim 1] ethylene-vinyl acetate copolymer saponification thing beyond degree of saponification 90 mol % of 20-60mol of ethylene content % and acetic acid vinyl unit (A) It is the number of end COOH bases (x) by an end adjustment agent. End CONRR'basis (-- however, R -- the hydrocarbon group of carbon numbers 1-22, and R' -- the number of H or hydrocarbon-group) of 1-22 (y) End adjustment polyamide system resin (B) adjusted so that $100xy/(x+y) \geq 5$ might be satisfied hindered phenol system compound (C) And aliphatic-carboxylic-acid alkaline-earth-metals salt (D) from -- becoming -- (A) (B) [a rate / a bulk density / 70:30-96:4] (A) (B) (C) to the total quantity comparatively -- 0.1 to 1 weight % -- (A) (B) (D) to the total quantity a rate -- metal conversion 0.5-15micromol/g it is -- ethylene-vinyl acetate copolymer saponification thing system resin constituent characterized by things.

[Claim 2] The co-extrusion layered product which allots an intermediate layer the layer of the resin constituent of Claim 1, and allots the layer of polyamide system resin to both outer layers.

[Claim 3] The co-extrusion layered product according to claim 2 whose polyamide system resin is the blend thing of nylon 6 and amorphous polyamide.

[Claim 4] The co-extrusion layered product according to claim 2 or 3 which is the packaging material which a co-extrusion layered product sterilizes [retort sterilization or / boil].

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the resin constituent which consists of an ethylene-vinyl acetate copolymer saponification thing and specific polyamide system resin, and the co-extrusion layered product containing the layer of the constituent.

[0002]

[Description of the Prior Art] Since the constituent of an ethylene-vinyl acetate copolymer saponification thing and polyamide system resin has the character in which the shock resistance based on the latter was given in the oxygen barrier nature, oil resistance, and solvent resistance based on the former, it is used for them by various uses including the film for food packing, the sheet, and the container. The co-extrusion layered product which allots an intermediate layer the layer of this constituent and allots the layer of polyamide system resin especially to both outer layers can expect the use as a packaging material in which retort sterilization or boil sterilization is possible.

[0003] In JP,S54-78749,A, they are 60 to 95 weight % of ethylene-vinyl acetate copolymer saponification things, KAPURO amide is made into a main constitutional unit, and the ratio of a methylene cardinal number to an amide cardinal number 5.2-6.5 The resin constituent which comes out and consists of 5 to 40 weight % of a certain fatty series copolymerization polyamide is shown.

[0004] In JP,S54-78750,A, they are 60 to 95 weight % of ethylene-vinyl acetate copolymer saponification things, The resin constituent which consists of 5 to 40 weight % of copolymerization polyamide which makes a KAPURO amide unit a main constitutional unit, and contains the constitutional unit of an aromatic series and/or alicycle fellows five to 50weight % is shown.

[0005] JP,S62-225535,A -- ethylene vinyl alcohol copolymer (a) And polyamide (b) (a) And (b) the [a solvent and the lth fellows of a periodic law table, or] -- using the water-soluble salt of II fellows metal After dissolving uniformly, the process of the ethylene vinyl alcohol copolymer constituent from which this solvent was removed is shown. the [the lth fellows of a periodic law table, or] -- the water-soluble salt of II fellows metal is chlorination lithium, a calcium chloride, chlorination magnesium, acetic acid calcium, acetic acid magnesium, etc.

[0006] It becomes JP,H4-76040,A from 60 to 95 weight % of ethylene-vinyl acetate copolymer saponification things, and 5 to 40 weight % of polyamide. And the melting point obtained by this polyamide having made carry out the copolymerization of KAPURO amide and at least two sorts of different fatty series polyamide irregularly is the thing of the range which is 120-200 degrees C. It is and is end carboxyl group content [X] further. And end amino group content [Y] [Y] < [X] The resin constituent with which it is satisfied (however, unit of [X] and [Y] mol/g and polymer) is shown in $+0.5 \times 10^{-5}$. Using the carboxylic acid of carbon numbers 2-23, Gia Min of carbon numbers 2-22, etc. as an amount adjustment agent of end groups is also shown.

[0007] It becomes JP,H4-178447,A from 60 to 95 weight % of ethylene vinyl alcohol copolymers, and 5 to 40 weight % of polyamide. And it is the fatty series polyamide with which this polyamide makes KAPURO amide a main constitutional unit, and the ratio of a methylene cardinal number to an amide cardinal number is satisfied of $5.20 \leq \text{CH}_2/\text{NHCO} \leq 6.50$, and an

end adjustment agent is used. End carboxyl group content [X] And end amino group content [Y] $[Y] < [X]$ The resin constituent whose melting point which adjusts $+0.5 \times 10^{-5}$ so that it may satisfy (however, unit of [X] and [Y] mol/g and polymer) is 160-215 degrees C is shown.

[0008] In Tokuganhei4-131237, they are the water vapor permeability of 40g/m2, and day. Resin outer layer (A) which has the above value 50 to 97 weight % of ethylene vinyl alcohol copolymer resin, 45 to 3 weight % of polyamide system resin, and metallic compounds of at least a kind of water solubility or alcoholic solubility Layer (B) of the constituent which consists of 0.005 to 5 weight % and the water vapor permeability of 20g/m2 and day Resin inner layer (C) which has the following values from -- the becoming gas barrier nature multilayer packing object is shown. They are the metallic compounds of water solubility or alcoholic solubility here, Specifically, they are chlorination lithium, lithium hydroxide, sodium chloride, sodium hydroxide, potassium chloride, water oxidization potassium, a calcium chloride, a calcium nitrate, an aluminium nitrate, ferric chloride, zinc chloride, sodium borate, acetic acid sodium, etc. Moreover, in this gazette, it is 2, 5-G t-butyl hydroquinone, 2, 6-G t-butyl p-cresol, 4, and 4-*****- (6-t-butylphenol) as an antioxidant, There is also a description that 2, 2'-methylene ****- (4-*****- 6-t-butylphenol), octadecyl 3-(3', 5'-G t-butyl 4'-hydroxyphenyl) propionate, 4, 4'-*****- (6-t-butylphenol), etc. may be added.

[0009] While having the at least three-layer composition which equips JP,H4-185322,A with a polyamide system resin layer, an ethylene-vinyl acetate copolymer **** ghost layer, and a polyamide system resin layer, said polyamide system resin layer in the multilayer film which is produced in the shape of a flat, and comes to carry out biaxial extension one by one -- much more as amorphous at least as 50 to 95 weight % of nylon 6 resin -- the multilayer film which is a mixed resin layer with 50 to 5 weight % of system polyamide system resin is shown.

[0010] In JP,H5-1819,B (JP,S62-22840,A) (i) an ethylene-vinyl acetate copolymer saponification thing and the number (A) of (ii) end carboxyl groups (-COOH) An end - CONRR' -- [machine] (-- however, R -- the hydrocarbon group of carbon numbers 1-22, and R' -- the number of hydrocarbon-group) of a hydrogen atom or carbon numbers 1-22 (B) a ratio -- $100x(B) / [(A) + (B)]$ The resin constituent which consists of polyamide system resin with which it is satisfied of ≥ 5 is shown. This gazette has reference also about the problem which the resin constituent of JP,S54-78749,A quoted previously and JP,S54-78750,A has.

[0011]

[Problem(s) to be Solved by the Invention] Although it is expected that the characteristic that each resin has the resin constituent which consists of an ethylene-vinyl acetate copolymer saponification thing and polyamide system resin will be employed efficiently, this resin constituent tends to generate gel at the time of fusion fabrication, and there is a problem on fabrication that long-run fabrication is difficult.

[0012] [polyamide / invention / invention of the gazette quoted upwards uses the

copolymerization polyamide and end regulation polyamide of a low-melt point point as polyamide system resin, or] [many] Although it is going to improve the problem of fabrication nature by devising performing preliminary mixture of both resin using a solvent, or using metallic compounds together etc., in addition from an industrial standpoint, there was room of improvement.

[0013] When carrying out usage which co-extrudes especially the resin constituent which consists of an ethylene-vinyl acetate copolymer saponification thing and polyamide system resin with the blend thing of nylon 6 and amorphous polyamide Since it becomes the fabrication under high temperature, such as temperature of 230-250 degrees C, it is necessary to attain perfect-ization of the occurrence prevention of gel, or thickening prevention with the passage of time.

[0014] [this invention] even if this invention is a time of carrying out usage which co-extrudes the resin constituent which consists of an ethylene-vinyl acetate copolymer saponification thing and polyamide system resin under such a background with the blend thing of nylon 6 and amorphous polyamide It aims at offering the resin constituent which can prevent effectively generating of gel, and thickening with the passage of time, and offering the co-extrusion layered product using such a resin constituent.

[0015]

[Means for Solving the Problem] [the ethylene-vinyl acetate copolymer saponification thing system resin constituent of this invention] ethylene-vinyl acetate copolymer saponification thing beyond degree of saponification 90 mol % of 20-60mol of ethylene content % and acetic acid vinyl unit (A) It is the number of end COOH bases (x) by an end adjustment agent. End CONRR'basis (-- however, R -- the hydrocarbon group of carbon numbers 1-22, and R' -- the number of H or hydrocarbon-group) of 1-22 (y) End adjustment polyamide system resin (B) adjusted so that $100xy/(x+y) \geq 5$ might be satisfied hindered phenol system compound (C) And aliphatic-carboxylic-acid alkaline-earth-metals salt (D) from -- becoming -- (A) (B) [a rate / a bulk density / 70:30-96:4] (A) (B) (C) to the total quantity comparatively -- it is 0.1 to 1 weight % -- (A) (B) (D) to the total quantity a rate -- metal conversion 0.5-15micromol/g it is -- it is characterized by things.

[0016] The co-extrusion layered product of this invention allots an intermediate layer the layer of the above-mentioned resin constituent, and allots the layer of polyamide system resin to both outer layers.

[0017] This invention is explained in detail below.

[0018] Ethylene-vinyl acetate copolymer saponification thing (A) If it carries out, the thing beyond degree of saponification 90 mol % (preferably 95mol % more than, still more preferably 98mol % more than) of 20-60mol of ethylene content % (preferably 25-55mol %) and acetic acid vinyl unit is used. Causing the fall of the too little ***** fabrication nature of an ethylene

content, the excess of an ethylene content causes the fall of oxygen barrier nature. When the degree of saponification is smaller than the above-mentioned range, the fall of oxygen barrier nature is caused. ethylene-vinyl acetate copolymer saponification thing (A) If it is little, it will not interfere, even if "copolymerization denaturation" is carried out by other KOMONOMA, such as an alpha olefin, an unsaturated-carboxylic-acid system compound, an unsaturated sulfonic acid system compound, acrylonitrile (meta), acryl amide (meta), vinyl ether, VCM/PVC, and styrene. Moreover, in the range which does not spoil the meaning of this invention, even if itizes [urethane-ization / ASETARU-] and ethylates [cyano-] "post-denaturation", it does not interfere.

[0019] End adjustment polyamide system resin (B) if it carries out It is the number of end COOH bases (x) by an end adjustment agent. The number (y) of end CONRR'bases (however, R the hydrocarbon group of carbon numbers 1-22 and R' H or the hydrocarbon group of 1-22) The polyamide system resin adjusted so that $100xy/(x+y) \geq 5$ might be satisfied is used.

[0020] Such end adjustment polyamide system resin (B) It is manufactured by carrying out heavy condensation of the polyamide materials under existence of mono-amine of carbon numbers 1-22 or the monocarboxylic acid of this and carbon numbers 2-23.

[0021] here -- as polyamide materials -- RAKUTAMU (epsilon-caprolactam --)

ENANTORAKUTAMU, capryl, lauryl RAKUTAMU, alpha-pylori boss, omega-amino acid (6-aminocaproic acid and 7-amino heptanoic acid --), such as alpha-PIPERIDON dibasic acid (adipic acid --), such as 9-amino nonanoic acid and 11-amino undecanoic acid Glutaric acid, pimelic acid, SUPERIN acid, azelaic acid, sebacic acid, UNDE can dione acid, dodeca dione acid, HEKISADE rudder-on acid, eicosa JIEN dione acid, Diethylene glycol acid, 2 and 2, 4-bird MECHIRU adipic acid, KISHIRI range carboxylic acid, 1, 4-cyclo HEKISAN dicarboxylic acid, terephthalic acid, isophthalic acid, etc., Gia Min (HEKISAMECHI range amine -- [, and]) [tetramethylen] [nonamethylene] Undecamethylene JIAMIN, dodeca methylene JIAMIN, 2 and 2, 4(or 2, 4, 4)-trimethylhexamethylene JIAMIN, ****- (4, 4'-amino cyclohexyl) methane, meta-KISHIRI range amine, etc. are raised.

[0022] as the mono-amine of carbon numbers 1-22 -- fatty series mono-amine (MECHIRU amine --) Ethyl amine, propylamine, a butylamine, pentylamine, HEKISHIRU amine, HEPUCHIRU amine, OKUCHIRU amine, 2-ethylhexyl amine, NONIRU amine, DESHIRU amine, UNDESHIRU amine, DODESHIRU amine, tridecyl amine, Tetradecyl amine, pentadecyl amine, hexadecyl amine, octadecyl amine, eicosyl amine, DOKOSHIRU amine, and alicyclic mono-amine (cyclohexyl amine --) aromatic series mono-amine (Ben Jill Amin --), such as methylcyclohexyl amine the second amine (N and N-JIMECHIRU amine --) of symmetry, such as beta-phenylethyl amine N and N-JIECHIRU amine, N, and N-JIPURO pill amine, N, and N-Vyv Chill Amin, N and N-JIHEKISHIRU amine, N, and N-JIOKUCHIRU amine, N, and N-JIDESHIRU amine etc., the second amine (N-*****- N-ethyl amine and an N-

*****- N-butylamine --) of mixture N-*****- N-DODESHIRU amine, N-*****- N-OKUDADESHIRU amine, N-ethyl N-hexadecyl amine, N-ethyl N-octadecyl amine, N-pro ****- N-hexadecyl amine, N-*****- N-cyclohexyl amine, N-*****- N-Ben Jill Amin, etc. -- etc. -- it is raised.

[0023] as the monocarboxylic acid of carbon numbers 2-23 -- fatty series monocarboxylic acid (acetic acid --) Propionic acid, butanoic acid, *****, caproic acid, enanthic acid, caprylic acid, Capric acid, pelargonic acid, undecanoic acid, lauryl acid, bird decanoic acid, Myristic acid, Miri Train acid, PAL methine acid, stearic acid, oleic acid, Alicyclic monocarboxylic acid (cyclohexane carboxylic acid, MECHIRU cyclohexane carboxylic acid, etc.), such as linoleic acid, arachin acid, and behenic acid, aromatic series monocarboxylic acid (benzoic acid, TORUIN acid, ethyl benzoic acid, phenylacetic acid, etc.), etc. are raised.

[0024] Moreover, if needed besides the above-mentioned mono-amine, or this and monocarboxylic acid fatty series Gia Min (ethylene diamine and trimethylene diamine -- [and]) [tetramethylen] Pentamethylene JIAMIN, HEKISAMECHI range amine, octa methylene JIAMIN, DEKAMECHI range amine, DEKAMECHI range amine, dodeca methylene JIAMIN, 2, 2, 4 (or 2, 4, and 4-) trimethylhexamethylene JIAMIN, etc., Alicyclic Gia Min (cyclo HEKISANJI amine, ****- (4, 4'-amino cyclohexyl) methane, etc.), aromatic series Gia Min (KISHIRI range amine etc.) and fatty series dicarboxylic acid (malonic acid --) KOHAKU acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, Sebacic acid, DODEKAN dione acid, TETORADE rudder-on acid, HEKISADE can dione acid, HEKISA decene dione acid, OKUTADE rudder-on acid, octadecene dione acid, Alicyclic dicarboxylic acid (1, 4-cyclo HEKISAN dicarboxylic acid, etc.), such as eicosa dione acid, eicosen dione acid, DOKOSAN dione acid, 2 and 2, and 4-bird MECHIRU adipic acid, aromatic series dicarboxylic acid (terephthalic acid, isophthalic acid, phthalic acid) Gia Min and dicarboxylic acid, such as KISHIRI range carboxylic acid Hitoshi, can also be made to live together.

[0025] End adjustment polyamide system resin (B) If in charge of manufacturing, the above-mentioned carboxylic acid and amine can be added using the above-mentioned polyamide materials in arbitrary stages until it begins the reaction under decompression from the reaction start time that what is necessary is just to start a reaction according to a usual state method. Moreover, you may add carboxylic acid and amine separately simultaneously.

[0026] The amount of carboxylic acid and the amine used as a quantity of the carboxyl group and an amine machine To 1mol (the monomer or 1mol of monomer units which constitute a repetition unit) of polyamide materials, respectively Two to 20 meq/mol, It is three to 19 meq/mol preferably (the amount of these of an amine machine makes 1Eq quantity of the amino group which reacts by 1Eq of carboxylic acid, and 1:1, and forms amide combination). It becomes impossible to manufacture the polyamide system resin which has the effect of this invention when remainder has little this quantity, and if too conversely large, it will become

difficult to manufacture polyamide with high viscosity, and it will come to have a bad influence on the physical properties of polyamide system resin.

[0027] The thing of the relative viscosity expected that reaction pressure is good to perform preferably 400 or less Torr of end of a reaction by 300 or less Torr, and its pressure of the end of a reaction is high is not obtained. Un-arranging does not have that pressure is especially low. Time of a decompression reaction It is good to usually consider it as about 1 to 2 hours for 0.5 hours or more.

[0028] End adjustment polyamide system resin (B) as a hydrocarbon group shown by R or R' in the -CONRR'basis which it has at the end an aliphatic hydrocarbon machine (a methyl group, an ethyl group, a propyl group, a butyl group, and a pentyl group --) A hexyl group, a heptyl group, an octyl group, a 2-ethylhexyl machine, a nonyl group, A decyl group, the Ung decyl group, a DODESHIRU machine, a tridecyl machine, a tetradecyl machine, A tetra-DESHIREN machine, a pentadecyl group, a hexadecyl machine, a heptadecyl machine, Alicyclic hydrocarbon machines (a cyclohexyl machine, a methylcyclohexyl machine, a cyclohexyl methyl group, etc.), such as an octadecyl machine, an eicosyl machine, and a DOKOSHIRU machine, aromatic hydrocarbon machines (a phenyl group, a toluyl machine, a benzyl group, beta-phenylethyl machine, etc.), etc. are raised.

[0029] end adjustment polyamide system resin (B) An end-COOH basis - CONRR' -- [the conversion rate to a machine] although adjusted by making amine, or this and carboxylic acid exist at the time of polyamide system resin manufacture in this invention -- the grade of this conversion -- the number of end-COOH bases (x) An end - CONRR' -- the number of machines (y) a relation -- $100xy/(x+y) \geq 5$ -- so that $100xy/(x+y) \geq 10$ may be satisfied preferably - A COOH basis - CONRR' -- being changed into the machine is desirable and, as for the quantity of -COOH basis which is not changed, it is [below 50microeq/g and polymer] preferably desirable that they are below 40microeq/g and polymer. When the grade of this conversion is small, un-[from the field of physical properties] arranging does not have it becoming impossible to expect the effect of this invention, and enlarging the grade of conversion conversely, but since it becomes difficult [manufacture], it is the best policy which the quantity of the end carboxyl group which does not denature limits to the grade used as 1microeq/g and polymer.

[0030] The hydrocarbon group shown by R and R' of the above-mentioned -CONRR'basis can measure polyamide system resin with gas chromatography after hydrolysis using chloride. - a COOH basis dissolves polyamide system resin in benzyl alcohol -- it can measure by titrating with 0.1N caustic alkali of sodium.

[0031] as the end group of polyamide system resin -- The above - CONRR' -COOH basis and -NH₂ originating in the above-mentioned polyamide materials other than a machine There is a machine.

[0032] Even if it has denatured about the end amino group and has not denatured, it does not interfere, but it is desirable for mobility and fusion heat stability to have denatured by the above-mentioned hydrocarbon group from the good thing.

[0033] Hindered phenol system compound (C) if it carries out N, an N'-HEKISA methylene screw (3, 5-G t-butyl 4-hydroxy hydronalium SHINNAMIDO), 1, 1, 3-tris (2-*****- 4-hydroxy 5-t-buthylphenyl) butane, 1, 3, 5-bird *****- 2 and 4, 6-tris (3, 5-G t-butyl 4-hydroxybenzyl) benzene, Tetrakis [methylene 3-(3', 5'-G t-butyl 4'-hydroxyphenyl) propionate], n-octadecyl beta-(4'-hydroxy 3', 5'-G t-buthylphenyl) propionate, 2 A 2'-methylene screw (4-*****- 6-t-butylphenol), 2 A 2'-methylene screw (4-ethyl 6-t-butylphenol), 4, 4'-CHIOBISU (6-t-butyl m-cresol), 4, 4'-CHIOBISU (3-*****- 6-t-butylphenol), pentaerythrityl tetrakis [3-(3, 5-G t-butyl 4-hydroxyphenyl) propionate], etc. are raised.

[0034] Aliphatic-carboxylic-acid alkaline-earth-metals salt (D) if it carries out The beryllium salt of with a carbon number of about one to nine aliphatic carboxylic acid, such as acetic acid, propionic acid, butanoic acid, *****, caproic acid, and capric acid, Magnesium salt, calcium salt, strontium salt, and barium salt are raised, and the magnesium salt and calcium salt of aliphatic carboxylic acid of carbon numbers 2-4 are especially important.

[0035] ethylene-vinyl acetate copolymer saponification thing (A) which described the resin constituent of this invention above End adjustment polyamide system resin (B) Hindered phenol system compound (C) And aliphatic-carboxylic-acid alkaline-earth-metals salt (D) from - it becomes.

[0036] It is (A) here. (B) A rate needs to be in the range of 70:30-96:4 at a bulk density. End adjustment polyamide system resin (B) When too little [a rate], it is an ethylene-vinyl acetate copolymer saponification thing (A). The improvement effects, such as boil-proof nature, do not fully show up. End adjustment polyamide system resin (B) When a rate is excessive, it is an ethylene-vinyl acetate copolymer saponification thing (A). The special feature of the oxygen barrier nature which it has, and others is spoiled.

[0037] Hindered phenol system compound (C) A rate is (A). (B) As opposed to the total quantity It is required to be in 0.1 to 1weight % of the range. Hindered phenol system compound (C) When there are few rates than the above-mentioned range, since antioxidizing nature runs short, it becomes easy to produce oxidizing quality gel during fabrication. On the other hand, even if the rate makes it more than the above-mentioned range, the control effect of oxidizing quality gel does not go up beyond a fixed limit, and becomes disadvantageous in cost.

[0038] Furthermore, aliphatic-carboxylic-acid alkaline-earth-metals salt (D) [a rate] (A) (B) as opposed to the total quantity -- metal conversion 0.5-15micro mol/g it is -- things are required, the rise of the too little ***** viscosity is caused, and the excess may produce generating and foaming of gel on the contrary at the time of fabrication, or may cause coloring of a film and

destabilization of fabrication nature

[0039] Additive agents, such as a plasticizer, stabilizer, a filler, colorant, lubricant, an antiblocking agent, and a spray for preventing static electricity, can also be blended with the above-mentioned resin constituent. Especially as lubricant, for example Ethylene screw fatty acid (carbon numbers 16-18) AMAIDO, It is desirable to blend higher-fatty-acid metal salt, such as higher-fatty-acid (carbon numbers 8-22) AMAIDO, polyethylene wax, polymer ester, fatty acid ester, and hydroxyfatty acid magnesium, zinc stearate, etc.

[0040] The above-mentioned resin constituent is fabricated by the form of a film, a sheet, a container, etc. by fusion fabrication. As a fusion molding method, arbitrary fusion molding methods including an extrusion-molding method (a blow-molding method and an extrusion coating method are included) and an injection-molding method are adopted.

[0041] The above-mentioned resin constituent is useful especially when obtaining a layered product by allotting this to an intermediate layer, and carrying out multilayer co-extrusion molding to them as polyamide system resin is arranged on both outer layers. Although various kinds of nylon including nylon 6, nylon 6 and 6, nylon 7, Nylon 11, and Nylon 12 is raised as polyamide system resin, especially the blend thing of nylon 6 and amorphous polyamide is important here. Other resin layer besides polyamide system resin can also be allotted to at least one side of both the outer layers.

[0042] The obtained co-extrusion layered product is useful as a packaging material in which retort sterilization or boil sterilization is possible.

[0043]

[Function] In this invention, it is an ethylene-vinyl acetate copolymer saponification thing (A). As the resin to blend End adjustment polyamide system resin (B) which is special polyamide system resin It uses and is hindered phenol system resin (C) as an auxiliary agent. Aliphatic-carboxylic-acid alkaline-earth-metals salt (D) It is using together.

[0044] Although the temperature at the time of fabrication serves as fabrication under the high temperature of 230-250 degrees C even if it is a time of carrying out usage which co-extrudes this resin constituent with the blend thing of nylon 6 with high molding temperature, and amorphous polyamide for that reason Generating of oxidizing quality gel and thickening with the passage of time are prevented effectively, and the long-run fabrication of them is attained.

[0045] Moreover, since the adhesion nature between layers is also notably improved when co-extruding this resin constituent with the blend thing of nylon 6 and amorphous polyamide, a DERAMI nation is not produced even if it presents retort sterilization and boil sterilization with the packaging material obtained by that co-extrusion.

[0046]

[Example] A work example is given below and this invention is explained further.

[0047] Work examples 1-6, a comparative example 1 - 6<end adjustment polyamide system

resin (B) Preparation>B-1 : In an autoclave, epsilon-caprolactam 60kg, Water They are 6.78meq to 1mol of epsilon-caprolactam about 1.2kg and octadecyl amine. After teaching so that it may become, sealing under nitrogen-gas-atmosphere mind, ****(ing) at 250 degrees C and reacting under 2-hour pressurization under churning, pressure is discharged, and it is 180Torr. What stopped churning, extracted the content as Strand, chip-ized it, carried out extraction removal of the unreacted monomer, and was dried by **** after having decompressed, having performed the reaction for 2 hours, introducing nitrogen subsequently and returning to normal pressure.

End COOH basis: 9microeq/g and polymer $100xy/(x+y) = 87$ [0048] B-2: They are 5.31meq and 5.30meq to 1mol of epsilon-caprolactam, respectively about octadecyl amine and acetic acid. Added, and end pressure of a polymerization reaction was set to 270Torr, and also it is B-1. What was manufactured like the case.

End COOH basis: 26microeq/g and polymer $100xy/(x+y) = 64$ [0049] B-3: They are 3.39meq and 3.39meq to 1mol of epsilon-caprolactam, respectively about octadecyl amine and stearic acid. Added, and end pressure of a polymerization reaction was set to 200Torr, and also it is B-1. What was manufactured like the case.

End COOH basis: 20microeq/g and polymer $100xy/(x+y) = 60$ [0050] Preparation> of materials besides < The following materials were prepared.

Ethylene-vinyl acetate copolymer saponification thing (A) A-1: Ethylene-vinyl acetate copolymer of degree [of 32mol of ethylene content % and acetic acid vinyl unit] % and melt index of saponification =3 (210 degrees C) [of 99.5mol] [0051] Hindered phenol system compound (C) C-1: N, N'-HEKISA methylene screw (3, 5-G t-butyl 4-hydroxy hydronalium SHINNAMIDO) (Ciba-Geigy "IRUGANOKKUSU 1098")

C-2: 1, 3, 5-bird *****. 2 and 4, 6-tris (3, 5-G t-butyl 4-hydroxybenzyl) benzene (Ciba-Geigy "IRUGANOKKUSU 1330")

C-3: Pentaerythrityl tetrakis [3-(3, 5-G t-butyl 4-hydroxyphenyl) propionate] (Ciba-Geigy "IRUGANOKKUSU 1010")

[0052] Aliphatic-carboxylic-acid alkaline-earth-metals salt (D) D-1: Acetic acid magnesium 4 hydration thing D-2: Calcium propionate D-3: Butanoic acid magnesium [0053] <Monolayer fusion fabrication> Above (C) An ingredient and (D) It is (A) about an ingredient. After adding for an ingredient, it cooled and pelletized, after carrying out fusion extrusion with a 2 axis extrusion machine or a single axis extrusion machine. Furthermore, (B) The extrusion machine equipped with T-Di after adding the ingredient and carrying out preliminary mixture by the Henschel mixer is supplied, fusion kneading is carried out, and it is 50 micrometers in thickness. The film was produced. Extrusion-molding conditions were set up as follows.
extrusion machine: -- diameter extruder screw [of 40mm]: -- full flight type extrusion
temperature: -- the extrusion machine temperature of 230 degrees C, and die temperature 250

degree-C screw-rotation-speed:40rpm [0054] <Co-extrusion molding> Chill roll through which a co-extrusion and cooling water circulate so that it may become the layer composition of Y/X/Y from T/Di who set the resin constituent of 90 weight % of nylon 6 resin, the polyamide system resin Y containing 10 weight % of amorphous polyamide, a work example, or a comparative example as the temperature of 250 degrees C It cooled and the flat-like three-layer film was obtained. Then, it extends 3 times with a 90-degree C roll drawing machine, and is the tenter drawing machine of 140 more-degree C atmosphere. Heat fixation was carried out in the atmosphere in 210 degrees C, making [extended, and] it about 4% of width reduce by this tenter continuously 3.5 times. The thickness of the obtained film was Y/X/Y=5/10/5 (micrometer).

[0055] <Evaluation criteria and valuation method> A fusion viscosity ratio KYAPI log rough (made by Oriental energy machine incorporated company) is used, and it is temperature [of 250 degrees C], and 122sec of shear rate-1. The viscosity η_{40} after stay and the viscosity η_{10} after the stay during 10 minutes were measured for 40 minutes under conditions, and it asked for the fusion viscosity ratios η_{40}/η_{10} at that time.

[0056] Heat deterioration of the pellet of a rate of gelling part class product was carried out under air atmosphere in gear oven for 250 degree-Cx 20 minutes, and it depended by Gyi acid insoluble, and asked for the rate of a gelling part. It is the case where the rate of a gelling part is less than 2% O and 2% or more ** and 2.5% or more of case were judged for less than 2.5% of case to be x.

[0057] Prolonged fabrication was performed in monolayer fusion fabrication of the long-run fabrication nature above, and long-run fabrication nature was judged in time for a gelling thing to come to appear on a film plane. The case of the work example 1 was made into O, and relative evaluation was made on ** and the thing which is clearly inferior for what is a little inferior to this like x.

[0058] The film appearance when being immersed in heat underwater on the conditions for 95 degree-Cx 30 minutes and the existence of the DERAMI nation were evaluated using the three-layer film obtained by co-extrusion molding of the boil-proof nature above. It is before and after processing and the case where there was no change in transparency and a DERAMI nation was not produced was judged to be O.

[0059] The film appearance when holding the three-layer film obtained by co-extrusion molding of the retort-proof nature above in 121-degree-C steam atmosphere for 30 minutes and the existence of the DERAMI nation were evaluated. It is before and after processing and the case where there was no change in transparency and a DERAMI nation was not produced was judged to be O.

[0060] <Conditions and result> The conditions of work examples 1-6 and comparative examples 1-6 and a result are shown in Tables 1-3. (C) The loadings of an ingredient are (A).

An ingredient and (B) As opposed to the total quantity of an ingredient. (D) a description of the clause of an ingredient -- the kind of alkaline-earth metals, and (A) An ingredient and (B) The amount of addition of the alkaline-earth metals to the total quantity of an ingredient (micromol/g) it is .

[0061]

[Table 1]

Work-example 1 work-example 2 work-example 3 work example 4 (A) ingredient A-1 90 copies A-1 80 copies A-1 70 copies A-1 70 copies (B) Ingredient B-1 Ten copies B-1 Copies [20] B-1 30 Copies B-1 Copies [30] (C) Ingredient C-1 4000Ppm C-3 4000 ppm C-2 4000ppm C-1 4000 ppm (D) Ingredient D-1 Mg 1.1 D-1 Mg 1.3 D-3 Mg 1.9 D-2 Ca 5.0 Fusion viscosity ratio 1.100.950.970.99 Rate of gelling part OO O O Long-run fabrication O O O O Boil-proof nature O O O O Retort-proof nature O O O O [0062]

[Table 2]

Work-example 5 work-example 6 comparative-example 1 comparative example 2 (A) ingredient A-1 90 copies A-1 90 copies A-1 80 copies A-1 80 copies (B) Ingredient B-2 Ten copies B-3 Copies [Ten] B-1 20 Copies B-1 Copies [20] (C) Ingredient C-2 4000Ppm C-1 4000 Ppm C-3 4000Ppm (D) Ingredient D-1 Mg 1.5 D-2 Ca 4.0 -- Fusion Viscosity Ratio 1.10.752.52.3 Rate [of Gelling Part] OO x ** long-run fabrication O O x x Boil-proof nature O O O O Retort-proof nature O O O O [0063]

[Table 3]

Comparative example 3 comparative-example 4 comparative-example 5 comparative example 6 (A) ingredient A-1 80 copies A-1 90 copies A-1 90 copies A-1 90 copies (B) Ingredient B-1 20 copies B-1 Copies [Ten] B-2 Ten Copies B-1 Copies [Ten] (C) Ingredient-C-1 4000Ppm C-2 500 ppm C-1 4000ppm (D) Ingredient D-3 Mg 1.5 D-1 Mg 18 D-2 Ca 4.0 D' Na 3.0 By fusion viscosity ratio 0.97 incapable-measurement 0.553.0 gelling, rate xO ** x Long-run fabrication ** x (discharge instability) x x Boil-proof nature O O O O Retort-proof nature O O O O (D' is acetic acid sodium)

[0064]

[Effect of the Invention] When carrying out usage depending on which the resin constituent of this invention co-extrudes this with the blend thing of nylon 6 with high molding temperature, and amorphous polyamide It comes out, and even if it is, although the temperature at the time of fabrication serves as fabrication under the high temperature of 230-250 degrees C, generating of oxidizing quality gel and thickening with the passage of time are prevented effectively, and the long-run fabrication of them is attained.

[0065] Moreover, since the adhesion nature between layers is also notably improved when co-extruding this resin constituent with the blend thing of nylon 6 and amorphous polyamide, a DERAMI nation is not produced even if it presents retort sterilization and boil sterilization with

the packaging material obtained by that co-extrusion.

[Translation done.]